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MOBILITY MONITORING OF TWO HERBICIDES IN AMENDED SOILS: A FIELD STUDY FOR MODELING APPLICATIONS

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Abstract

This paper reports the mobility and total balance of chlorotoluron (CTL), flufenacet (FNC) and bromide ion (Br^-) throughout a sandy soil profile after the application of spent mushroom substrate (SMS) and green compost (GC). Obtaining mobility dataset is crucial to simulate the herbicides' fate under amended soil scenarios by application pesticide leaching models with regulatory application (FOCUS models). The application of organic residues is nowadays increased to improve the crop yields and there is a gap in the simulations of this kind of amended scenarios. A two-year field experiment involving unamended soil (S) and SMS- or GC-amended soil plots was conducted. CTL, FNC, and Br^- were annually applied and their residual concentrations were determined in soil profiles (0-100 cm) regularly sampled. In all the treatments the order of mobility is followed as FNC < CTL < Br^-. SMS and GC increased herbicide retention in the top 10 cm by the higher organic carbon (OC) content than the unamended soil, and their ability to increase the soil's water-holding capacity and to decrease water percolation. Simultaneously dissolved organic carbon (DOC) content facilitated herbicide transport being it favoured by the initial soil moisture content and the rainfall shortly after the chemicals' initial application. Over the first year, residual amounts (<2.6%) of Br^-, CTL and FNC were leached down to 90-100 cm depth in the three treatments. However, over the second year low CTL and FNC amounts (<1.0%) reached the bottom layer only in S+SMS although high Br^- concentrations did so in the three treatments (<20%). According to the total balance of Br^-, CTL, and FNC in the soil profiles other processes (degradation, mineralization, bound residues formation, and/or crop uptake) different from leaching below 1 m depth might play a key role in their dissipation especially in the amended soil profiles. SMS and GC are likely to be used as organic amendments to preserve the soil and water quality but in the case of

SMS, its higher DOC content could imply a higher potential risk for groundwater contamination than GC.

Keywords: leaching, chlorotoluron, flufenacet, bromide tracer, soil profile, experimental amended plots

1. Introduction

Different strategies are being applied in agriculture today to increase crop yields and obtain the corresponding benefits. The use of pesticides and the application of organic residues to the soil as organic amendments are two such strategies. The losses in the crop yield due to the non-application of pesticides can be as high as 40% (AEPLA, 2019). The impact of the use of organic amendments on the crop yield is based on the amount of nutrients and the addition of OM on the soil and on their ability to maintain the soil's properties and, therefore, its fertility (Ingelmo Sánchez and Rubio Delgado, 2008; Yazdanpanah et al., 2016). Both agricultural practices are fully compatible, and often organic amendments and pesticides coexist in the soil. However, their combination can have significant environmental impacts, as the main processes governing the fate of pesticides (adsorption-desorption, degradation, mobility, etc.) may be modified in the presence of organic residues, with their solid OC and/or DOC content playing a key role (Yang et al., 2005; Marín-Benito et al., 2012a; 2016; López-Piñeiro et al., 2013).

Pesticide mobility changes in amended soils have especial interest because they can reach the groundwater leading to contamination not foreseen (Postigo et al., 2010). In addition, the evaluation of their environmental risks under amended soils is not considered over the pesticide registration tests. Changes in pesticide mobility have been

51 frequently assessed in presence of organic wastes of different origins (urban, livestock,
52 agricultural, and agro-industrial activities). In most cases, these studies have been
53 carried out under laboratory conditions (Kodešová et al., 2012; Marín-Benito et al.,
54 2013; Álvarez-Martín et al., 2017), and less frequently so at field scale (Cabrera et al.,
55 2009; Herrero-Hernández et al., 2015; Marín-Benito et al., 2018). Working at laboratory
56 scale involves doing this under controlled conditions geared towards target variables.
57 This allows reaching relevant conclusions about the influence of individual variables,
58 such as the application of organic amendments to soils on a selected process (e.g.,
59 pesticide mobility). Nevertheless, and as opposed to field studies, their extrapolation is
60 limited because they are not representative of real conditions, where the interaction of
61 multiple variables informs a different behaviour to that observed one under laboratory
62 studies (Ahmad et al., 2003; Herrero-Hernández et al., 2015).

63 Accordingly to this, the need for more robust conclusions on the impact that
64 organic amendments have on pesticide mobility calls for field-scale trials that allow
65 compiling wide dataset including real pesticide concentrations in the soil profile. These
66 dataset would allow the calibration and validation of pesticide leaching models in
67 amended soils. Then, they could be used as a tool for the prediction of the
68 environmental fate of pesticides under amended soil conditions and for the optimization
69 of pesticide application jointly with organic amendments aimed to avoid the water
70 pollution. Modelling studies based on amended soil scenarios are rarely due to the lack
71 of complete dataset as it is proposed in this paper (Boesten and van der Pas, 2000;
72 Filipović et al., 2014).

73 A representative scenario was chosen in the Spanish region of Castilla and Leon
74 to evaluate herbicide mobility under amending agricultural practices at field scale. This
75 location is vulnerable to pesticide contamination, consisting of a soil with a

predominantly sandy texture, low in OM content and with continuous cereal cropping. The assays involved two herbicides with different mobility behaviour: CTL and FNC. They are widely used to control broad-leaved weeds and grasses in the pre- and post-emergence of wheat crops. Wheat (*Triticum* spp.) was selected because it is one of the most widely grown crops worldwide (OECD-FAO, 2019).

CTL is a phenylurea that is fairly soluble in water and records a moderate persistence in the soil, low hydrophobicity, and a high potential for leaching (EC, 2005; PPDB, 2019), as evidenced by its frequent presence in surface, ground and drinking waters (Chilton et al., 2005; Fingler et al., 2017; Casado et al., 2019). CTL degradation leads mainly to the formation of desmethylchlorotoluron in soil, which persistence and mobility are similar to that of the parent compound (PPDB, 2019).

FNC is an oxyacetamide moderately soluble in water, with high adsorption in the soil. This herbicide has a higher hydrophobicity and persistence in soil than CTL, but a lower leachability (PPDB, 2019). FNC has also been detected in surface waters (Casado et al., 2019), while it is unlikely to leach to groundwater (Gajbhiye and Gupta, 2001; Novohatska et al., 2018), hence this may depend on weather conditions, the time lapse between the application date and the first precipitation event, and soil properties (USEPA, 1998; Milan et al., 2015; Willkommen et al., 2019). However, FNC degrades in the soil mainly into two metabolites, flufenacet oxoacetic acid (FNC-OA) and flufenacet oxoethanesulfonic acid (FNC-ESA), with a higher or much higher potential, respectively, for leaching to groundwater than FNC (EC, 2003; PPDB, 2019).

The mobility behaviour of CTL in soil has been studied mainly in undisturbed and hand-packed soil columns under laboratory conditions, as well as in outdoor lysimeter experiments (Renaud et al., 2004; Walker et al., 2005; Navarro et al., 2012; Langeron et al., 2014). However, there are hardly any studies involving CTL transport

under field conditions (Kodešová et al., 2004; Chilton et al., 2005; Kočárek et al., 2010). In turn, and to the best of our knowledge, the effect of organic amendments on the mobility of this herbicide has been assessed in a somewhat unusual manner, involving only packed soil cores under controlled laboratory conditions (Kodešová et al., 2012). By contrast, only a handful of studies have been published on FNC mobility in soil (Rouchaud et al., 1999; Vasilakoglou et al., 2001; Milan et al., 2015; Willkommen et al., 2019), and none including amended soils.

Therefore, the aims of this paper are to assess: i) the mobility and the total balance of the herbicides CTL and FNC, and of the Br^- tracer ion through an unamended and SMS and GC amended soil profile, and ii) the effect that two organic residues, SMS and GC, have on the environmental fate of these herbicides. Real concentrations of Br^- and herbicides and volumetric soil water content were obtained at different times over two years throughout a field experiment to obtain a complete dataset. This dataset is necessary for the subsequent simulation of the environmental fate of the herbicides with FOCUS pesticide leaching models (those used for pesticide registration purposes at European level according to recommendations of the FOrum for Co-ordination of pesticide fate models and their Use group) under amended soil scenarios.

2. Materials and Methods

2.1. Chemicals and organic amendments

The field study used the commercial formulations Erturon® (chlorotoluron 50% w/v, Cheminova Agro S.A., Madrid, Spain), and Herold® (flufenacet 40% w/v, Bayer Crop Science S.L., Valencia, Spain). Analytical standards of both herbicides (> 99.5% purity) were supplied by Sigma Aldrich Química S.A. (Madrid, Spain). The major metabolites of both herbicides, desmethylchlorotoluron, FNC-ESA sodium salt, and

126 FNC-OA (> 99.3% purity, Sigma) (PPDB, 2019) were also analysed throughout the
127 experiment. These compounds' characteristics are presented in Supplementary Material
128 Table S1 (PPDB, 2019). Conservative tracer transport using Br^- as an ion tracer (KBr,
129 99.8% purity) was applied to describe the dispersive characteristics of the unamended
130 and amended soil systems for the herbicide mobility study.

131 The SMS from *Agaricus bisporus* and *Pleurotus ostreatus* (2:1) cultivation and
132 the GC from the pruning of plants and trees in parks and gardens were supplied
133 following an aerobic composting process by Sustratos de la Rioja S.L. (Pradejon, Spain)
134 and Viveros El Arca S.L. (Salamanca, Spain), respectively. The main characteristics of
135 both organic residues were determined in air-dried and sieved (< 2 mm) samples (Table
136 S2) using the methods included in Supplementary Material.

137

138 **2.2. Experimental set-up, sampling and processing of soil profiles**

139 A two-year (2016-2018) field experiment was set up at the Muñovela
140 experimental farm belonging to the Institute of Natural Resources and Agrobiology of
141 Salamanca, Spain (40º54´15´´N latitude and 5º46´26´´W longitude). The soil was a
142 Eutric-Chromic Cambisol **(**IUSS Working Group WRB, 2015) with sandy-loam (0-90
143 cm depth) and a sandy-clay (90-160 cm depth) texture (Table S3). The experimental
144 layout consisted of randomised complete blocks including nine experimental plots of 9
145 m × 9 m, with three treatments and three plot replicates per treatment, corresponding to
146 unamended soil (S), soil amended with spent mushroom substrate (S+SMS), and soil
147 amended with green compost (S+GC). SMS and GC were applied to the soil at rates on
148 a dry weight basis of 140 and 85 t ha^{-1}, respectively. A rototiller was used to incorporate
149 the organic amendments into the top 20 cm in November 2016. Before the chemicals
150 (herbicides and Br^- ion tracer) were applied, three soil profiles (one per treatment) were

opened in three additional plots for the pedological characterization of soil profile in the field site. Soil samples were taken from each one of the five observed horizons of their respective soil profiles after 30 days of organic residue application. Soil samples were air-dried, sieved (< 2 mm), and their physicochemical characteristics determined as indicated in Supplementary Material (Table S3).

Polyvinyl chloride (PVC) pipes with hermetically sealed bases (120 cm length × 5.2 cm Ø) were installed in each one of the experimental plots (one pipe per plot) for regular monitoring of the volumetric soil water content in sections of 20 cm from the surface down to 1 m using a portable Troxler Sentry 200-AP electrical probe (Troxler International Ltd., NC, USA). All the plots were annually cropped with winter wheat and managed according to best agricultural practices. After the harvest, the soil was maintained bare during the fallow period. The field experiment ended on 30 Nov. 2018.

CTL, FNC, and the Br^- tracer were sprayed once per crop cycle at 15, 5, and 53 kg a.i. ha^{-1}, respectively, under the commercial formulations previously indicated. The chemicals were applied jointly in pre-emergence using a sprayer attached to a tractor on 1 Dec. 2016 and on 13 Nov. 2017 (346 days after the first application). According to the experimental farm's records, none of the chemicals assayed had ever been applied to the experimental field, as an initial onsite background analysis did not detect any residues.

Rainfall and minimum and maximum air temperature were recorded throughout the experiment at an onsite weather station operated by the Spanish Agency of Meteorology.

The chemicals' mobility assessment involved sampling unamended, SMS- and GC-amended soil profiles at 1, 17, 33, 60, 80, 151, 229, and 339 days after their first application, and after 1, 29, 64, 127, 142, 181, and 225 days after their second application (corresponding to 347, 376, 411, 474, 489, 528, and 572 days). At each

sampling time, five 100-cm soil cores (of 3-cm inner diameter) were randomly sampled in each plot and sectioned into 10 segments, each with a 10-cm thickness. Representative average soil samples of each plot were obtained by mixing the five subsamples corresponding to the same depth. Composite samples were put into plastic bags and transported in portable refrigerators to the laboratory, where they were homogenised and sieved (< 2 mm) for their analysis. The amounts of CTL, FNC and Br^- determined were expressed as percentages of the initial amount. The pH, OC and DOC values were determined at different times after the chemicals' applications to assess their influence on herbicide mobility.

The adsorption capacity of CTL and FNC for each unamended and SMS- and GC-amended soil horizon was determined as a single-point concentration (1 μg mL^{-1}) at the beginning of the experiment through the joint use of the active ingredients of both herbicides, and with 6 ºC as the working temperature, replicating that registered in the field at the time of herbicide application. The distribution coefficients (K_d) were calculated as indicated in Marín-Benito et al. (2019) (Table S4).

2.3. Chemical extraction and analysis

The extraction and analysis of herbicides and their major metabolites formed during the experiment was carried out as indicated in Marín-Benito et al. (2019). Triplicate subsamples of moist soil (6 g) from each 10-cm segment of unamended or amended soil cores taken at each sampling time were extracted with acetonitrile and the herbicides and their metabolites were determined by HPLC-DAD-MS using a Waters chromatograph (Waters Assoc., Milford, USA). Extraction efficiencies and quality indicators of detailed analytical method are included in Supplementary Material.

200 Br^- concentrations were determined following the same method as described for
201 the herbicides, albeit using deionised water as extractant and without the concentration
202 step. They were quantified using a Metrohm Ion Chromatograph (Metrohm Ltd.,
203 Switzerland) with a conductivity detector.
204
205 **2.4. Meteorological conditions over the field experiment**
206 Rainfall and air temperature data were recorded throughout the two experimental
207 periods (Fig. 1). The first experimental period ran from 1 Dec. 2016 to 12 Nov. 2017
208 (346 days), and the second one from 13 Nov. 2017 to 30 Nov. 2018 (382 days). The
209 average air temperature in both periods was similar, ranging from -3.8ºC to 27ºC and
210 from -3ºC to 27.6ºC, respectively. However, differences in average air temperature and
211 precipitation regime were recorded between both periods, and this played an important
212 role in chemical mobility through the soil profile. The average air temperature was
213 higher for the first period (13.1ºC) than for the second one (11.6ºC). Accumulated
214 precipitation at the end of first period was 273.2 mm compared to 525.4 mm recorded
215 over the entire second period, with their respective average intensity being 2.5 and 2.8
216 mm h^{-1}. There were only seven major rainfall events (> 10 mm) during the first period
217 (Fig. 1a), which was characterized by intensive rainfall in winter and less so in spring
218 and summer. Seventeen rainfall events higher than 10 mm were recorded during the
219 second period. The winter and spring in this latter period were especially wet for the
220 geographical area of study whose average annual rainfall is about 400 mm (Fig. 1b).
221
222 **3. Results**
223 **3.1. Assessment of soil profile characteristics over time**

Temporal variation of the parameters pH, OC and DOC was determined as they can be modified by adding organic residues and they can affect the behaviour of herbicides in soils (Thevenot et al., 2009; Marín-Benito et al., 2013, 2018) (Data Analysis is described in Supplementary Material). A significant increase ($p < 0.01$) in the mean pH values of S topsoils (6.28-7.13) was observed after treatment with the organic residues (7.33-7.54 in S+SMS and 7.37-7.81 in S+GC) at different sampling times in the first experimental period (Fig. S1).

When adding the organic residues, the OC contents for the S topsoil (0.79-0.75%, mean 0.77±0.02) increased to 2.61-2.22% (mean 2.44±0.16) in the S+SMS and to 1.87-1.65% (mean 1.78±0.09) in the S+GC over the entire experimental period (range 10-572 days after the application of herbicides) (Fig. S1). ANOVA analysis indicated significant differences between OC mean values in all the samples (S+SMS > S+GC > S, $p<0.001$), depths ($p<0.001$) and times ($p< 0.01$). The OC content in S was constant down to 40 cm, decreasing below this depth, and no significant changes were observed over time. In amended soils, the OC mean values decreased down to 50 cm, but they increased 3.17-1.22 times (S+SMS) and 2.31-1.07 times (S+GC) in relation to S at 10-50 cm. The increase in soil OC content by the SMS or GC effect was maintained at the different depths throughout the two-year experiment, therefore it indicates that the application of these residues to the soil could improve long-term soil properties.

The DOC contents ranged between 0.12-0.48 mg OC g^{-1} soil (mean 0.33±0.14) for the S topsoil and they increased to 0.50-0.79 mg OC g^{-1} soil (mean 0.65±0.15) (S+SMS) and to 0.38-0.72 (mean 0.54±0.16) (S+GC) over different times (Fig. S1). Significant differences were found between the mean DOC values of amended and unamended soils (S+SMS = S+GC > S, $p<0.001$), depths ($p<0.001$), and times

($p<0.001$). In the amended soils, the mean DOC values decreased down to 50 cm although they increased 1.98-1.39 times in S+SMS, and 1.65-1.47 times in S+GC in relation to S, in the different soil layers from 10 to 50 cm. In general, these DOC contents increased throughout the whole experiment, being significantly different in S+SMS ($p<0.001$) and in S+GC ($p<0.001$) (Fig. S1).

3.2. Soil water content profiles over time

Soil water content was recorded every 20 cm down in the soil profiles (0-100 cm) at different times throughout the experiment (a total of 38 times). Fig. 2 restricts the information available on the moisture profiles to five selected times per experimental period. During the first experimental period, the soil water content at a depth of 0-20 cm followed the order S (0.100–0.184 $m^3\ m^{-3}$) < S+GC (0.155–0.244 $m^3\ m^{-3}$) < S+SMS (0.196–0.279 $m^3\ m^{-3}$) (Fig. 2) at different sampling times according to the soil OM content. The standard deviation of the mean values at each depth and replicate plots was < 14%, indicating homogeneity and close agreement between plots with the same treatment (Fig. 2). A sharp increase in soil moisture down to a depth of 40 cm at different treatment times was recorded by the unamended soil profile (control) together a continuous decrease with depth which only increased seven months later. In the second experimental period, the soil water content followed a similar trend as in the first one. It increased in the top 20 cm in the order S (0.136–0.232 $m^3\ m^{-3}$) < S+GC (0.145–0.260 $m^3\ m^{-3}$) < S+SMS (0.149–0.251 $m^3\ m^{-3}$), and in the three treatments increased at different sampling times at 80-100 cm (Fig. 2).

3.3. Mobility of ion bromide in unamended and amended soil profiles

The distribution of Br^- in the S, S+SMS, and S+GC profiles (0-100 cm) at different sampling times after their application (Fig. 3) revealed that the tracer was not mobile below 0-10 cm at the initial sampling time for both experimental periods when ~100% of applied dose was recovered in the topsoil. However, 3-10 days after its first application, Br^- mobility in S was observed down to 50 cm (2-4% of the amount applied). The tracer ion reached a depth of 100 cm 33 days after its application (< 0.5%), and it was detected throughout the entire soil profile up to 229 days. After two months, Br^- concentrations in the topsoil decreased to 50% of the amount applied, and varied between 5-17% down to 60 cm and < 1% in the deepest soil layers (60-100 cm) five months after application. Br^- was still recorded from 0 to 70 cm eleven months after its application showing peak concentrations of 13-11% at 10-30 cm (339 days), but no presence or concentrations below its detection limit were observed after 70 cm. A total balance of $Br^- \approx 100\%$ was maintained in the S profile up to 80 days after application, indicating no mobility below 1 m. Br^- concentrations progressively decreased over time, and the total balance was < 40% 339 days after application.

Br^- mobility in both amended soils was detected mainly in the top 30 cm two months after the first application. Br^- concentrations (> 12%) below 30 cm were detected only 80 days after its application, and residual concentrations (< 1%) reached the bottom layer (90-100 cm) at 151 days in both treatments. Br^- was still found 339 days after its application from 0 to 90 cm (S+SMS) and from 0 to 60 cm (S+GC), with a peak concentration of 8-18% at 10-30 cm. The total Br^- balance in the amended soil profiles was < 80% from one month after application, and it decreased to 40-44% at the end of the first experimental period (339 days), as it was also observed in the S treatment.

297 The dynamics of Br^- through the soil profiles changed over the second
298 experimental period. Following the application of the respective chemicals (Fig. 1) it
299 recorded almost twice as much rainfall as the first, being 2.5 times higher than in the
300 two first months. A more relevant displacement of the Br^- through the S profile was
301 observed during these two months and a Br^- peak of 66% was recorded at 30-50 cm,
302 with decreasing concentrations in the range 16 - 1% at 60-100 cm. From the second to
303 the fourth months the high accumulated rainfall (164.8 mm, Fig. 1b), with seven rainfall
304 events between 10.2 and 26 mm, contributed largely to the movement of high
305 concentrations of Br^- (10-18%), which remained below 2% in the top 50 cm. Br^- peaks
306 in the 60-100 cm layers (11-24%) were recorded five months after the second
307 application, and at the last sampling time (225 days) this peak was recorded at 70-100
308 cm, with a concentration range of 14-18%. A total balance of $Br^- \approx 100\%$ was
309 maintained in all the soil profiles up to 64 days and then, when Br^- recorded a residual
310 percentage of 40-64% in the soil profiles, it decreased progressively from 127 days (53-
311 78%) to 225 days.
312
313 **3.4. Mobility of chlorotoluron in unamended and amended soil profiles**
314 The CTL concentrations in the soil profiles (0-100 cm) after the first and second
315 applications were determined at different times in S, S+SMS and S+GC and expressed
316 as percentages of the amount initially applied (Fig. 4). Initial CTL concentrations
317 determined in the unamended and amended topsoil layer corresponded to ~100% of the
318 applied dose. In S, an increase in herbicide concentrations in the soil layers down to 40-
319 50 cm (after 17 days) or down to 1 m (from 33 to 229 days after application) was
320 observed. After two months, a decrease in CTL concentration in the topsoil (remaining
321 amount < 56% of that applied) was followed by a progressive decrease over time

through the end of the first experimental period (339 days, < 15%). In general, peak concentrations were always detected in the top 20 cm (Fig. 4). The application of SMS and GC to soil increased significantly the mean remaining amounts of CTL in the topsoil over the sampling time (S+SMS = S+GC > S, $p < 0.02$), while decreasing them in the soil profile (Fig. 4). At the end of the first experimental period (339 days), higher concentrations of CTL were detected in the top 10 cm of S than of S+SMS or S+GC (S > S+SMS = S+GC, $p<0.01$) and residual concentrations were observed down to 40 cm in S and S+SMS, and down to 20 cm in S+GC (Fig. 4). The total CTL balance remained ≥ 100% in the S profile up to 60 days after its application, and up to 80 days in S+SMS and S+GC. This percentage decreased to 20% (S), 8% (S+SMS), and 11% (S+GC) 339 days after their application.

Like Br^-, the CTL leaching dynamics observed in the second experimental period was different (Fig. 4). The residual amounts of CTL decreased quickly in the S topsoil to 55% of the initial amount only one month after its application, and it decreased to ≈ 2% six months later. The application of the organic residues to soil decreased the CTL residual amounts in the S+SMS profile over the whole second period. In S+GC, they decreased two months after herbicide application, with its behaviour then being similar to the one observed in the S+SMS. Significant differences among the mean residual amounts in soil profiles were observed at 20-40 cm (S > S+SMS=S+GC, $p < 0.01$), and no CTL residues were observed in the amended soils below this depth. The total CTL balance in the soil profile remained ≥ 100% in the S+GC treatment 29 days after its application, varying between 65-71% in S and S+SMS. These percentages decreased to 3.98% (S), 0.91% (S+SMS), and 0.58% (S+GC) at the last sampling time (225 days), when residual concentrations of CTL were

346 detected at 30, 20 and 10 cm in S (0.35%), S+SMS (0.24%), and S+GC (0.58%),
347 respectively.
348
349 **3.5. Mobility of flufenacet in unamended and amended soil profiles**
350 Initial FNC concentrations determined in the top 10 cm of the three soil
351 treatments corresponded to ~100% of the applied dose. The FNC concentrations
352 determined at different times (Fig. 5), indicated the herbicide mobility in S with
353 increasing concentrations detected down to 30 cm (from 17 to 33 days after application)
354 or down to 60 cm (after 60 days), although no herbicide was recorded down to 1 m in
355 this period as indicated for CTL. The maximum depth reached by FNC was observed
356 after 80 days with residual concentrations (< 1%) detected in the deepest S layers (70-
357 100 cm). At this time, a decrease in FNC concentration was observed in the topsoil
358 (remaining amount < 50% of that applied) followed by a progressive decrease over time
359 through to the end of the first experimental period (7%). The peak concentrations were
360 always observed in the top 10 cm (Fig. 5). The residual amounts of FNC increased in
361 the topsoil after SMS and GC application over the sampling time (S+SMS = S+GC > S,
362 $p < 0.009$), as previously observed for CTL (Fig. 4 and 5). FNC concentrations at this
363 depth ranged from 80% to 94% in the amended soils for the 17 to 80-day period.
364 However, herbicide concentrations were higher in S than in the amended soils below 10
365 cm although differences were not significant ($p<0.10$). FNC was detected in the whole
366 S+SMS profile 33 days after its application, while the maximum depth reached by FNC
367 in S+GC was observed at 151 days, when residual concentrations (< 1%) were detected
368 in the soil layers from 30 to 100 cm.
369 FNC persistence was higher in the topsoils than that of CTL in the first
370 experimental period, with dissipation of the herbicide ≈ 50% in S after 80 days and after

151 days in S+SMS and S+GC. However, FNC dissipation increased over time and similar residual amounts of herbicide were found in the top 10 cm in all three treatments (S 7.03%, S+SMS 7.92%, S+GC 2.65%) after the first experimental period. At the end of this period (339 days), FNC was detected at 10-20 cm in S and S+GC, and down to 30 cm in S+SMS.The total FNC balance in the soil profiles recorded the same behaviour as CTL, remaining $\geq$ 100% in the S treatment up to 60 days after its application, and up to 80 days in both amended soils. After 339 days of application, this percentage decreased to 12% (S), 10% (S+SMS), and 5% (S+GC), following the same order as CTL.

As observed for CTL, the residual amounts of FNC determined in the S topsoil indicated a decrease in herbicide retention during the second experimental period, considering similar sampling times to those in the first period, and its mobility was detected only down to 50-60 cm (Fig. 5). The application of SMS and GC generally increased the residual amounts of FNC in the surface horizons of S+SMS and S+GC (S < S+GC = S+SMS, $p < 0.004$). Nonetheless, the residual amounts of FNC were increased in the next soil layer (10-20 cm) and in all the soil treatments compared to the first period.

Contrary to CTL, FNC dissipation increased progressively in all the soils over time, and no significant decrease in their total balance was observed in any of the soils two months after herbicide application and with a high accumulated rainfall (68.4 mm). Like CTL and unlike Br^-, after this rainy period, no relevant displacements of the maximum peak of FNC to deep soil horizons were observed in any soil treatment (Fig. 5). This means FNC behaviour in the soils was similar to that one observed over the first period. However, FNC never reached the deepest soil layer (90-100 cm) in S or S+GC. The maximum depth this herbicide reached during the second experimental

period was 60 cm in S and 80 cm in S+GC 181 days after its application, whereas the compound reached 90-100 cm in S+SMS 127 days after its application. The total FNC balance in the soil profiles varied between 67-100% in S and S+SMS up to 142 days after its application, and after 181 days in S+GC. These percentages decreased to 26% (S), 36% (S+SMS), and 32% (S+GC) after 225 days (the last sampling time during the second experimental period), and they were higher than those for CTL (Fig. 4 and 5). Marín-Benito et al. (2019) reported similar results for FNC applied in the same soils under laboratory conditions at the end of an incubation period of 273 days.

4. Discussion

4.1. Changes in soil water content profiles over time

A logical downward water movement over time was described for explaining the percolation behaviour, in line with the precipitations recorded. The application of SMS and GC to the soil into the top 20 cm increased this layer's water-holding capacity, and influenced the water (and chemicals) dynamics in all the amended soil profiles. The organic amendments regulated the percolation rate to deeper layers and a more regular and continuous movement of water was promoted from the topsoil toward deeper layers over time (Ingelmo Sánchez and Rubio Delgado, 2008). The movement was not as abrupt and slower than observed in the unamended soil. This meant that the sections from 20 to 40 cm or even to 60 cm in the amended soils tended to record higher soil water content than the ones corresponding to the unamended soil, and did so for longer time period. This also explains why the soil water content observed at a depth of 0-20 cm, following the order S < S+GC < S+SMS, increased (S) or decreased (S+SMS and S+GC) at a depth of 80-100 cm at different sampling times. Changes in soil porosity, aggregation state, pore size and connectivity, water-holding capacity, and hydraulic

conductivity induced by the presence of organic amendments rich in OM have been reported (Ingelmo Sánchez and Rubio Delgado, 2008; Yazdanpanah et al., 2016; Marín-Benito et al., 2018) revealing their ability to modify water dynamics.

Compared to the first experimental period, higher soil water contents were recorded at 80-100 cm as a result of a rainy period that drove percolation down to deeper soil layers in the second year of experimentation. This effect was observed especially in the unamended soil, showing again how SMS and GC can regulate the percolation. However, the organic amendments' impact on the soil water content profiles was minimised compared to that of the high rainfall recorded between 64 and 127 days after the second application (Fig. 1b). This high rainfall (164.8 mm) homogenised the percolation behaviour in both unamended and amended soil profiles.

4.2. Mobility of ion bromide in soil profiles: Influence of soil water content

The mobility of Br^- down to the deepest soil horizons was fast and probably enhanced by the soil's high moisture in the top 40 cm at the application date (53.6 mm of rainfall were recorded in the previous 27 days, including 34.2 mm in the last 11 days, being compounded by an already rainy autumn) and by the rainfall accumulated in the 15 days after the application (21 mm) (Fig. 1a). Some authors have reported rainfall's major influence on overall leachate losses in the period shortly after the application of chemicals (Walker et al., 2005; Willkommen et al., 2019). The Br^- behaviour in both amended soils indicated lower mobility than that in S and it is consistent with the slower water percolation observed in these soils through the soil profile, as previously indicated

A hypothetical loss of Br^- by leaching below 1 m linked to the accumulated rainfall of 203.4 mm from 80 to 339 days could be responsible for the low Br^- balances after 80 days. However, its low concentration (< 2%) below 60 cm 151 days after its

446 application and the peak concentrations always upper than 40 cm do not seem to
447 support this hypothesis. Other Br^- sinks could play an important role in the loss of the
448 total balance in the soil including its uptake by wheat plants. This hypothesis is
449 supported by Shtangeeva et al. (2016) investigations on uptake and accumulation of
450 large amounts of Br^- in roots and leaves of wheat plants through a phytoextraction study
451 that includes soils contaminated with KBr.

452 The dynamics of Br^- changed over the second experimental period because it
453 was wetter. An important loss of Br^- by leaching below 1 m was suggested, in contrast
454 to one observed during the first period although S now recorded a similar behaviour to
455 both amended soils. As previously indicated, the important rainfall events recorded
456 between 64 and 127 days after the second application are likely to be homogenised
457 water percolation and Br^- behaviour in the three soil treatments, minimising the effects
458 of the organic amendments. Nevertheless, the lowest total balances of Br^- were again
459 recorded generally in the amended soil profiles, albeit with smaller differences than
460 those previously observed.

461

462 **4.3. Mobility of chlorotoluron in soil profiles as affected by different processes**

463 A fast mobility of the herbicide to deeper soil horizons was observed in the S
464 profile in a similar way to the one indicated previously for Br^-. CTL is a polar
465 compound slightly soluble in water, and it may be easily transported through the sandy-
466 loam soil profile after its application in wet soil and the rainfall events 15 days later
467 (Walker et al., 2005) (Fig. 1a). In general, a greater washing of CTL in S than in the
468 amended soils occurred in the whole soil profile, however no significant differences
469 were observed at any depth. These results are consistent with the adsorption coefficients
470 of CTL by soils from 0-10 cm (0.773 (S), 4.773 (S+SMS), and 2.563 (S+GC) (Table

S4), and the relation between herbicide adsorption and initial OC in the soils (increasing in the order S < S+GC < S+SMS, Fig S1) which has also been reported to other phenylurea compounds (Cabrera et al., 2007; Hiller et al., 2008; Kodešová et al., 2012; Rodríguez-Cruz et al., 2012). The dissipation of CTL in the surface soil increased in all the treatments over time and the herbicide was simultaneously detected in the entire soil profiles 33 days after its application.

In amended soils, CTL mobility was reduced relative to the unamended soil by the water-holding capacity of the 20 cm topsoil layers increased with the SMS and GC application (S 0.230 m^3 m^{-3}, S+SMS 0.290 m^3 m^{-3}, S+GC 0.260 m^3 m^{-3}), which would decrease water percolation in relation to S (Fig. 2) (Marín-Benito et al., 2018). On the other hand, CTL mobility through the unamended and amended soil profiles depends on the properties of each soil layer, mainly OC and DOC contents. These are the main soil parameters influencing herbicide behaviour in soil (Thevenot et al., 2009; Marín-Benito et al., 2013, 2018), and they were modified by the addition of organic residues as previously indicated in section 3.2. In fact, a significant correlation coefficient was found between residual concentrations of CTL and OC content in the amended soil profile after 10, 80, and 229 days, for S+SMS ($r = 0.902$-0.975, $p < 0.05$), and S+GC ($r = 0.880$-0.954, $p < 0.01$) and it was not significant for S ($r = 0.559$-0.759, $p < 0.1$). OC content was lower in the S profile than in the S+SMS and S+GC profiles down to 50 cm (Fig. S1), and it could explain the mobility and presence of herbicide residues at all depths up to 229 days after their application, while they were only detected in S+GC and S+SMS up to 60 and 151 days, respectively.

CTL leaching dynamics was closer to that detected for Br^- in S than in the amended soils. The lowest total CTL balance in the amended soil profiles could be explained by a greater leaching of compound below a depth of 1 m or a higher

degradation in these soil profiles. In our study, DOC content was higher in amended soils than in unamended soil down to 50 cm and increased over time (Fig. S1). DOC content could affect the behaviour of CTL controlling the sorption/desorption of the herbicide as reported by Song et al. (2008) and enhancing its mobility. Yang et al. (2005) have also observed greater CTL adsorption in soils without DOC. The leaching of another phenylurea herbicide, diuron, was also promoted in amended soils, most likely due to the formation of diuron-DOC mobile complexes (Thevenot et al., 2009).

The influence of OC and DOC of S+SMS or S+GC on the CTL residual amounts was explored through soil profiles by a multiple correlation analysis considering jointly data down to 50 cm after 10, 80 and 229 days. The equations obtained: CTL% = 3.13 – 985 DOC(%) + 42.7 OC(%) ($p = 0.001$) in S+SMS, and CTL% = -6.99 – 1258 DOC(%) + 62.8 OC(%) ($p = 0.002$) in S+GC explained 66% and 59% of the CTL residual amounts in the respective amended soil. These equations indicate that DOC had a higher negative effect (mobility increasing) than the positive effect (adsorption increasing) of OC on CTL residual amounts. No significant results were found for S. The results indicated that in the amended soils CTL could remain adsorbed by the soil OC or remain in solution adsorbed by DOC, enhancing the mobility and/or the degradation of the herbicide by microorganisms (Marín-Benito et al., 2012b). The CTL degradation process was consistent with the detection of a CTL metabolite (desmethylchlorotoluron) (Table S1) in the top 10 cm of the soils over the entire first experimental period (339 days) (S+SMS (2.8%) < S+GC (10.6%) < S (23.5%) (Fig. S2) and it was not found below 30 cm in any soil treatment (data not shown). The formation of this metabolite was previously revealed under laboratory conditions at 6 ºC (Marín-Benito et al., 2019).

520 Other additional dissipation pathways, such as CTL mineralisation and/or the
521 formation of bound residues by the parent herbicide, could also have occurred
522 simultaneously to CTL leaching (EC, 2005) and support the low total balance of
523 herbicide obtained. Both dissipation pathways would have been facilitated in the
524 S+SMS and S+GC soils by the presence of a higher content of both DOC (more
525 herbicide in solution) and OC (higher adsorption of herbicide in the topsoil),
526 respectively, compared to S, as observed for other pesticides (Marín-Benito et al.,
527 2012b). Finally, it is important to stress that the uptake by wheat roots has been reported
528 as a sink for CTL and other phenylureas (Song et al., 2008; Pascal-Lorber et al., 2010).
529 The scope of this uptake process could be also controlled by DOC content (Song et al.,
530 2008) and affect the total CTL balance although it was not evidenced in this paper.
531 After the second experimental period with higher rainfall, the presence of CTL
532 was higher in the S profile than in S+SMS and S+GC, again indicating a greater
533 leaching of CTL in S than in the amended soils. Unlike the first period, no significant
534 correlation between the residual amounts of CTL, and OC and DOC contents in S+GC
535 profile was found for the second period, and it was of little significance in the S+SMS
536 profile (R^2 = 22.8%, p = 0.084). The variable soil water content did not improve the
537 multiple correlations obtained with OC and DOC for explaining the residual amounts of
538 CTL. These results indicate that CTL dissipation after the second application and under
539 a higher rainfall regime was faster than after the first one, as previously indicated for
540 this and other herbicides under field conditions (Rouchaud et al., 2000; Marín-Benito et
541 al., 2018). The CTL dissipation was more explained by degradation rather than by
542 mobility process, especially in the amended soils. The higher DOC content recorded in
543 all the soil profiles in the second period could enhance the amount of CTL in solution,
544 and its availability for the biodegradation. The presence of desmethylchlorotoluron was

545 also detected in the three soil treatments assayed, again being detected mainly in the top
546 10 cm. The total amounts of metabolite formed at this depth over the entire second
547 period (225 days) followed the same order as the first period: S+SMS (4.9%) < S+GC
548 (7.1%) < S (9.0%) (Fig. S2).
549
550 **4.4. Mobility of flufenacet in soil profiles as affected by different processes**
551 FNC mobility in soil profiles was low as also reported by Rouchaud et al. (1999)
552 in a sandy loam with 2.2% of MO, although the results in our experiment indicated that
553 this compound could reach the groundwater in highly permeable soils (USEPA, 1998).
554 The application of SMS and GC to the soil enhanced the residual amounts of FNC as
555 previously observed for CTL (Fig. 4 and 5) but FNC persistence was higher in the
556 topsoils than that of CTL in the first experimental period. FNC is more hydrophobic
557 than CTL, and this could explain this compound's higher persistence in soils (PPDB,
558 2019). The data are in accordance with the adsorption coefficients of FNC by soils from
559 the 0-10 cm layer determined in the laboratory (1.038 (S), 6.340 (S+SMS), and 2.909
560 (S+GC), Table S4). Herbicide adsorption by topsoils was consistent with their initial
561 OC, which increased in the order S < S+GC < S+SMS (Fig. S1) (Gajbhiye and Gupta,
562 2001). FNC mobility was reduced in amended soils as that of CTL by its adsorption by
563 soil OC. A positive relationship between residual concentrations of FNC at 10, 80 and
564 229 days after treatment and OC content in the soil profile was found in the amended
565 soils. Nevertheless, increasing the ageing time in the soil could increase FNC mobility,
566 with this process being favoured by the high accumulated rainfall (39 mm) from 80 to
567 151 days after its application or by the soil DOC content. A significant multiple
568 correlation was found between residual concentrations of FNC, and the OC and DOC
569 contents when jointly considering data down to 50 cm after 10, 80 and 229 days in

570 S+SMS (FNC% = – 6.13 – 844 DOC(%) + 44.6 OC(%) (R^2 = 72.6, p = 0.0002) and in
571 S+GC (FNC% = – 17.5 – 1111 DOC(%) + 67.3 OC(%) (R^2 = 59.3, p = 0.002). These
572 correlations corroborate again the negative or positive influence of DOC and OC,
573 respectively, on herbicide residual amounts as observed for CTL. No significant results
574 were found for S. The variable soil water content did not improve the multiple
575 correlations obtained with OC and DOC for explaining the residual amounts of FNC.

576 The lowest total FNC balance observed in the amended soil profiles at the end of
577 the first experimental period could be attributed either to a greater leaching of
578 compound below 1 m or to a higher degradation of the compound in these soil profiles,
579 both enhanced by their higher DOC, as previously explained. However, the presence of
580 the two main metabolites of FNC (FNC-ESA and FNC-OA) was not relevant in any of
581 the three soil profiles over the entire first experimental period. These metabolites were
582 detected in a dissipation study under laboratory conditions with topsoil samples taken *in*
583 *situ* from the experimental plots (Marín-Benito et al., 2019). Only the FNC-OA
584 metabolite was detected, and its presence was observed mainly in the topsoil of the
585 three treatments at different sampling times, but always at concentration levels below
586 the limit of–quantification (LOQ). As reported previously for CTL, other dissipation
587 pathways could also have occurred and to a greater extent in the amended soils.
588 Mineralisation and the formation of non-extractable bound residues were reported for
589 FNC after 100 days varying between 10.2-31.9% and between 6.0-56.2%, respectively
590 (EC, 2003). Like CTL, FNC uptake by the wheat plants could be an additional sink for
591 this herbicide, although no related studies have been found.

592 During the second experimental period, the residual amounts of FNC in the S
593 topsoil decreased as observed for CTL but the residual amounts of FNC increased in the
594 next soil layer (10-20 cm) and in all the soil treatments compared to the first period.

595 DOC and the higher amount of rainfall accumulated during the second experimental
596 period explained this greater residual amount of FNC detected in all the 10-20 cm
597 sections. FNC leaching pattern in the soils was similar to that one observed over the
598 first period. However, it was detected that the losses of FNC below 1 m were null in S
599 and S+GC due to leaching process, and were non relevant in S+SMS due to the low
600 amounts of herbicide detected at this depth over the experimental period (Fig. 5). DOC
601 could favour herbicide mobility in the amended soils after the second application, as
602 previously indicated for the first period, or its degradation. In fact the FNC-OA
603 metabolite was again detected mainly in the topsoil for the three treatments at different
604 sampling times, but always at lower concentrations than the LOQ.
605
606 **4.5. Remarks on the environmental role of organic amendments in herbicides**
607 **mobility**
608 The effect of SMS and GC on the mobility of the herbicides CTL and FNC and
609 the Br- tracer in a sandy soil was assessed over a 2-year field experiment. SMS and GC
610 increased the water-holding capacity of the 20-cm topsoil affecting percolation and
611 leaching of chemicals. However, in unamended and amended soils the rapid mobility of
612 chemicals was initially more affected by the rainfall events recorded shortly after their
613 first application than by the high rainfall recorded. SMS and GC increased the soil OC
614 and DOC with opposite effect on the herbicides' dynamics. While the soil OC enhanced
615 the herbicides' adsorption and/or persistence in the upper soil layers decreasing their
616 downward mobility (especially for the most hydrophobic herbicide FNC), the soil DOC
617 enhanced the herbicides' transport to deeper soil horizons and their bioavailability to be
618 degraded (especially for CTL). Residual Br^- and herbicides amounts leached down to 1
619 m in all the treatments over the first period while during the second period large

amounts of Br^- leached down to 1 m in the three treatments and only residual amounts of herbicides (< 1% of the amount applied) reached the deepest soil layer in S+SMS. A total balance of both herbicides in the soil profile at the end of both experimental periods was not in accordance with the amounts leached below 1 m depth in all treatments. It indicates that other processes different from mobility (degradation, mineralization, formation of non-extractable bound residues, and/or crop uptake) could be involved in the dissipation of the herbicides, especially in the amended soils. The degradation was one of the possible dissipation pathways and it was confirmed by the detection of herbicide metabolites, mainly of CTL.

5. Conclusions

The results obtained show that the application of SMS and GC to soil could reduce groundwater contamination by these herbicides by enhancing the adsorption. However, DOC from amendments have to be considered to optimize the amendment doses applied because of its higher DOC content could imply a higher potential risk for groundwater contamination as observed here for SMS relative to GC. Additional studies (now in progress) supported on the dataset obtained in this paper will be carried out for simulations with FOCUS pesticide leaching models. These models integrate the main processes involved in the dynamics of pesticides in the soil and allow predicting possible water contamination and consequently to adopt and assess preventive strategies to avoid it when an amendment is applied.

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806

Figure Captions

Fig. 1. Rainfall and average temperature monitored over first (a) and second (b) experimental period.

Fig. 2. Mean values of soil water content monitored for each 20-cm depth in unamended (S) and SMS- and GC-amended (S+SMS and S+GC) soils at different sampling times after the herbicides' application (above graphics correspond to the first application and below graphics correspond to the second application). Error bars represent the standard deviation of mean values of plots treated (n=3).

Fig. 3. Distribution profiles of bromide in unamended (S) and SMS- and GC-amended (S+SMS and S+GC) soils at different sampling times after the bromide application (above graphics correspond to the first application and below graphics correspond to the second application). Error bars represent the standard deviation of mean values of plots treated (n=3).

Fig. 4. Distribution profiles of chlorotoluron in unamended (S) and SMS- and GC-amended (S+SMS and S+GC) soils at different sampling times after the herbicide application (left graphics correspond to the first application and right graphics correspond to the second application). Error bars represent the standard deviation of mean values of plots treated (n=3).

Fig. 5. Distribution profiles of flufenacet in unamended (S) and SMS- and GC-amended (S+SMS and S+GC) soils at different sampling times after the herbicide application (left graphics correspond to the first application and right graphics correspond to the second application). Error bars represent the standard deviation of mean values of plots treated (n=3).

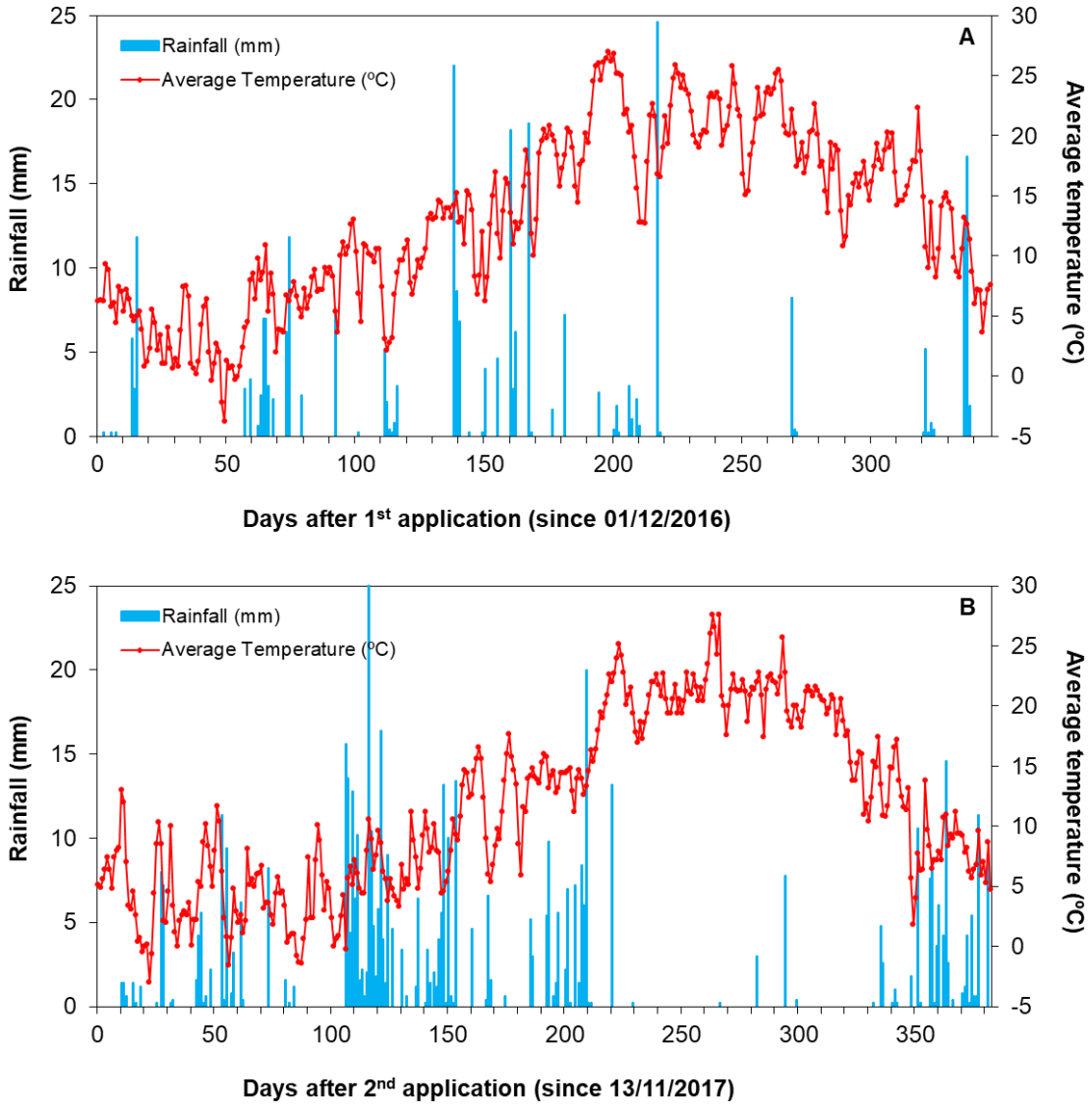
A
Rainfall (mm)
Average Temperature (°C)
Rainfall (mm)
Average temperature (°C)
Days after 1st application (since 01/12/2016)
B
Rainfall (mm)
Average Temperature (°C)
Rainfall (mm)
Average temperature (°C)
Days after 2nd application (since 13/11/2017)

Fig. 1.

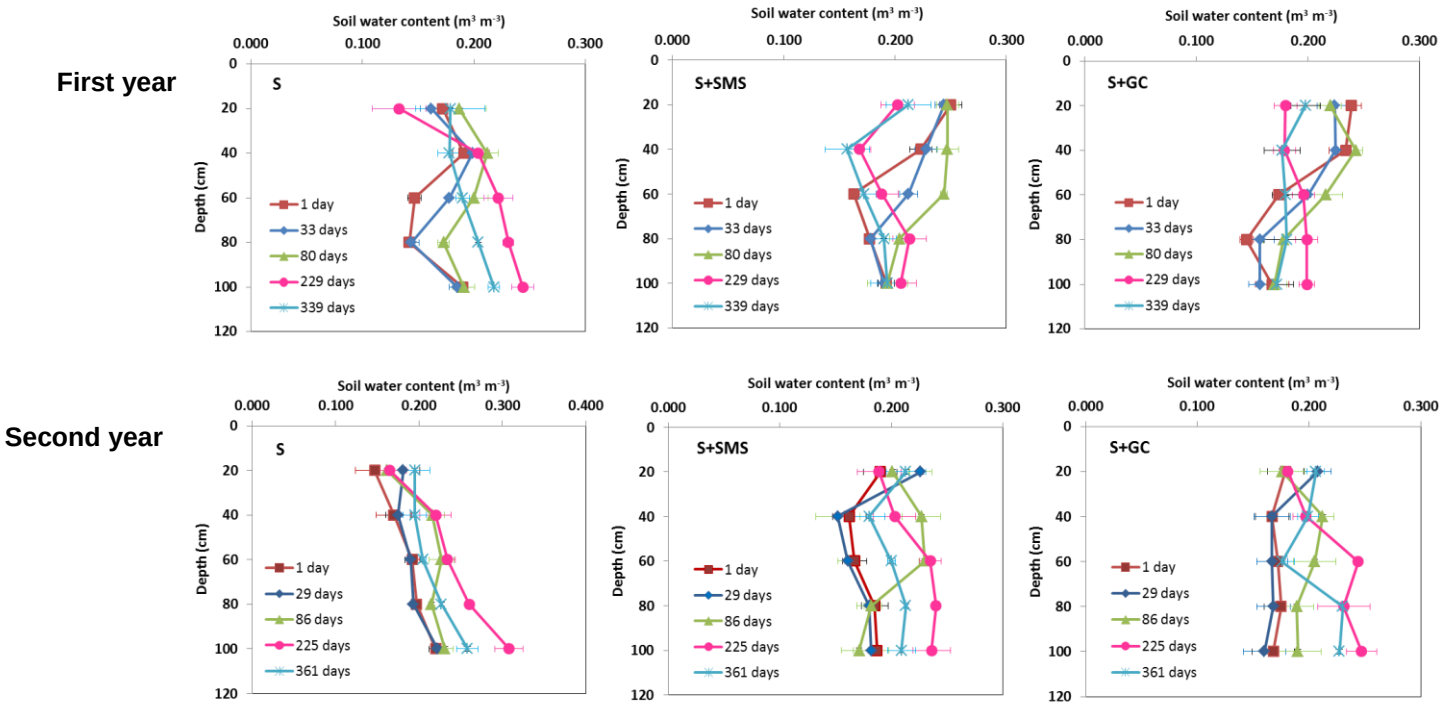
First year
Second year
S
S+SMS
S+GC
Soil water content (m³ m⁻³)
Depth (cm)
1 day
33 days
80 days
229 days
339 days
29 days
86 days
225 days
361 days

Fig. 2.

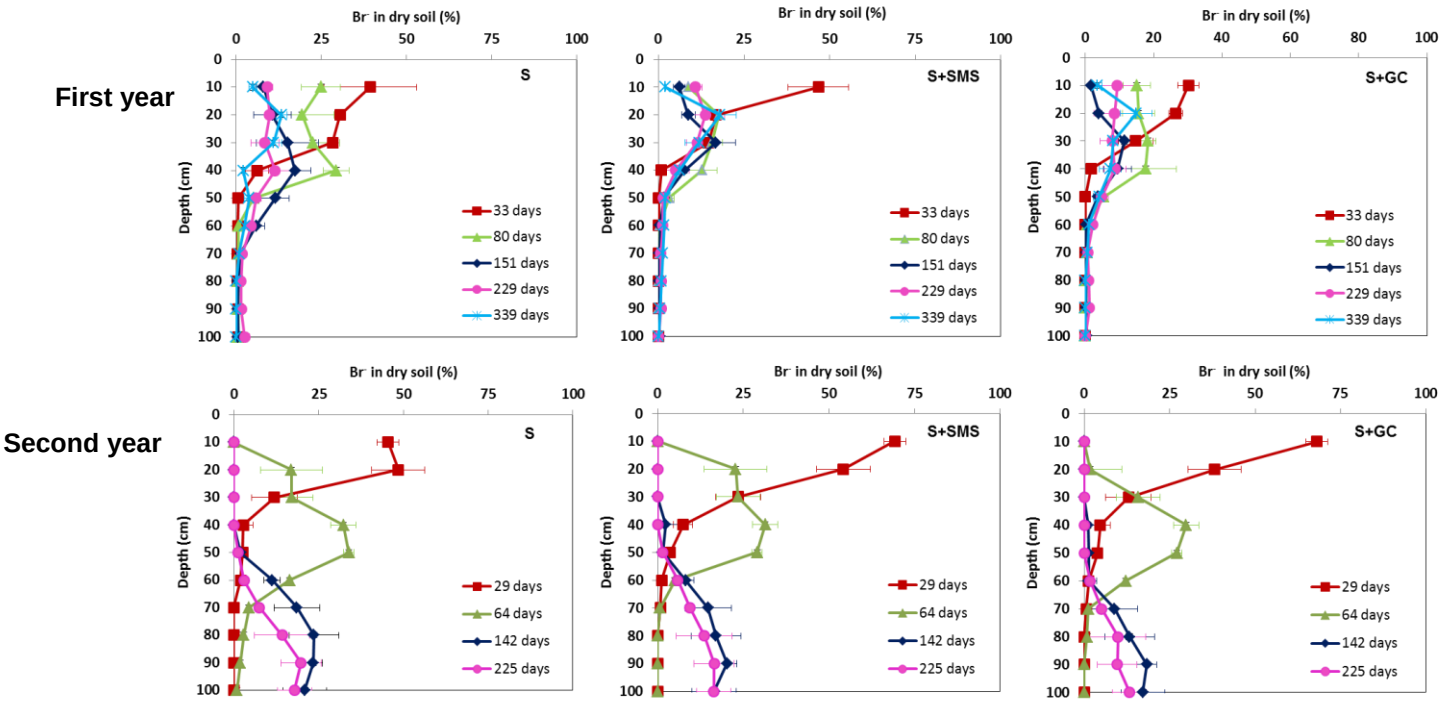
First year
Second year
Br⁻ in dry soil (%)
Depth (cm)
S
S+SMS
S+GC
33 days
80 days
151 days
229 days
339 days
29 days
64 days
142 days
225 days

Fig. 3.

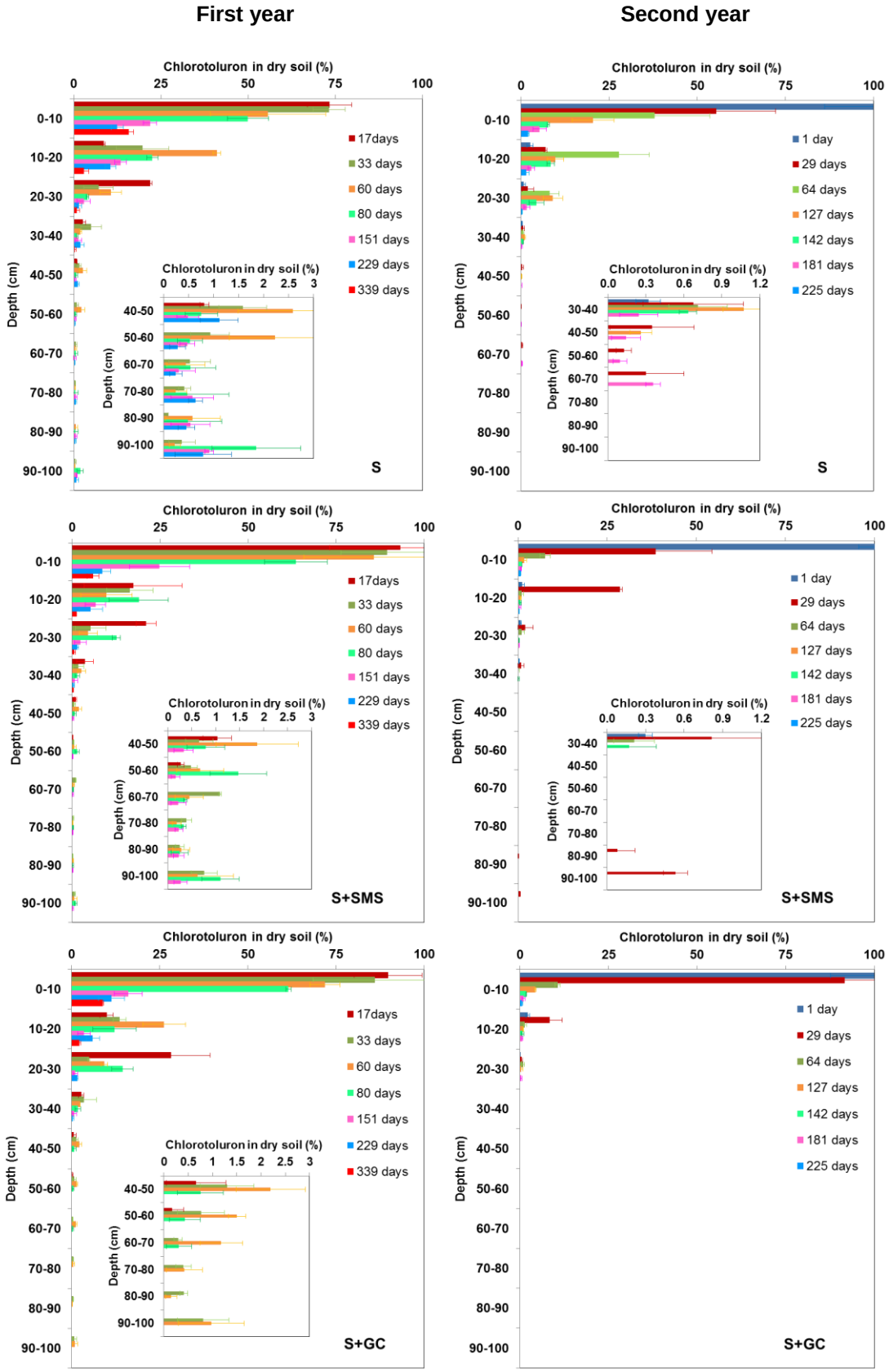
First year
Second year
Chlorotoluron in dry soil (%)
Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
70-80
80-90
90-100
17days
33 days
60 days
80 days
151 days
229 days
339 days
1 day
29 days
64 days
127 days
142 days
181 days
225 days
S
S+SMS
S+GC

Fig. 4.

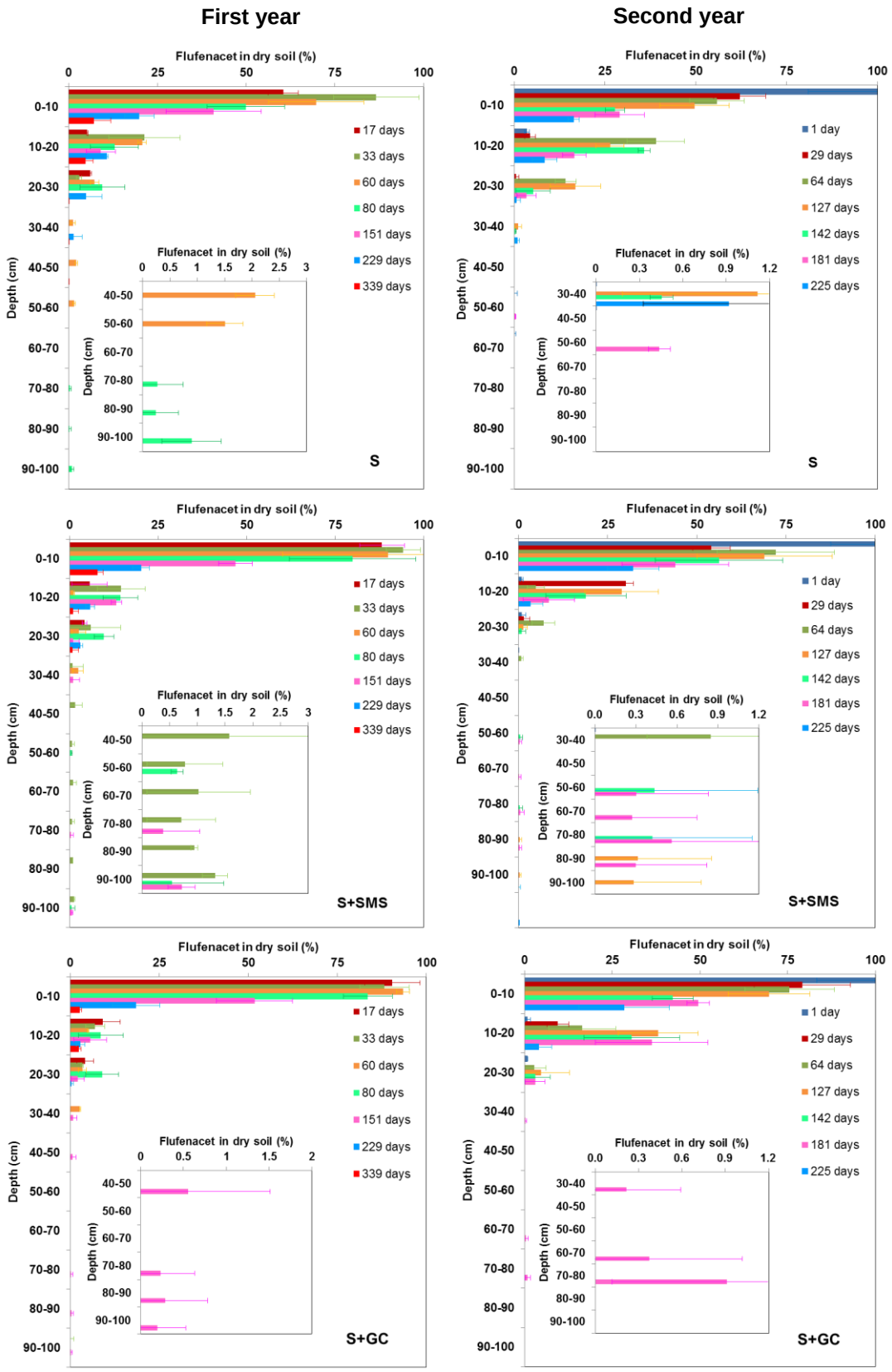
First year
Second year
Flufenacet in dry soil (%)
Depth (cm)
17 days
33 days
60 days
80 days
151 days
229 days
339 days
1 day
29 days
64 days
127 days
142 days
181 days
225 days
S
S+SMS
S+GC

Fig 5.

SUPPLEMENTARY MATERIAL

MOBILITY MONITORING OF TWO HERBICIDES IN AMENDED SOILS: A FIELD STUDY FOR MODELING APPLICATIONS

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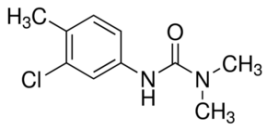
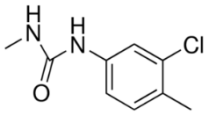
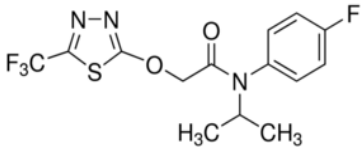
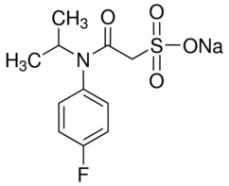
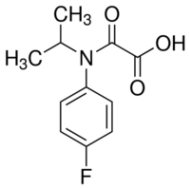
Number of Tables: 4
Number of Figures: 2

Materials and Methods

Table S1. Main characteristics of herbicides and their metabolites.

Common name Chemical structure	IUPAC name	WS[a] (mg L^{-1})	Log Kow[b]	Koc/Kfoc[c] (mL g^{-1})	DT_{50}[d] (days)	GUS index[e]
Chlorotoluron 	3-(3-chloro-p-tolyl)-1,1-dimethylurea	74	2.5	196	59	3.02
Desmethylchlorotoluron 	3-(3-chloro-p-tolyl)-1-methylurea	-	-	248	60	2.84
Flufenacet 	4'-fluoro-*N*-isopropyl-2-[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yloxy]acetanilide	51	3.5	273.3	19.7	2.02
Flufenacet-ESA 	2-(4-fluoro-*N*-propan-2-ylanilino)-2-oxoethanesulfonic acid	5500	-	12.5	302	7.20
Flufenacet-OA 	((4-fluorophenyl) (isopropyl)amino) oxoacetic acid	-	-	14.0	11.1	2.98

[a] Water solubility at 20ºC; [b] Octanol/water partition coefficient at pH 7 and 20ºC; [c] Sorption coefficient normalized to organic carbon content; [d] Time to degradation 50% of compound; [e] Gustafson mobility index (PPDB, 2019)

Experimental

Characterization of Organic Amendments

The pH and the electric conductivity were determined in a residue/water suspension (1/2.5 and 1/5 w/v ratio, respectively). The electric conductivity was determined using a conductivimeter LF91 (WTW, Weilheim, Germany). Organic matter (OM) content was calculated as 100-% ash being ash percentage determined by weight difference after ignition at 540°C for 24 h. Dissolved organic carbon (DOC) was determined in a residue/ water suspension (1/100 w/v ratio) after shaking (24 h, 20°C), centrifuging (20 min at 10,000 rpm) and filtering (< 0.45 μm). The DOC content was determined using a Shimadzu 5050 (Shimadzu, Columbia, MD, USA) organic carbon analyzer. Total OC and N were determined using a LECO CN628 (LECO Corporation, Saint Joseph, MI) elemental analyzer. Assimilable P was determined by the Olsen method while assimilable K, Ca and Mg were extracted with ammonium acetate at pH 7 and quantified using a Varian model 720-ES inductively coupled plasma-optical emission spectrometer (Varian Instruments, Palo Alto, CA).

Table S2. Characteristics of the organic amendments spent mushroom substrate (SMS) and green compost (GC) (% dry weight basis).

Parameter/Organic amendment	SMS	GC
pH	7.9	7.2
electric conductivity (S/m)	0.78	0.22
ash (%)	40.6	54.0
moisture (%)	37.7	48.6
OM[a] (%)	59.4	46.0
DOC[b] (mg g^{-1})	11.88	7.184
OC[c] (%)	35.0	26.7
N (%)	2.3	1.1
C/N	15.2	24.3
CEC[d] ($cmol_c\ kg^{-1}$)	35.1	41.4
P_2O_5 (mg/100g)	59.5	40.3
K_2O (mg/100g)	858	458
CaO (mg/100g)	1774	757.3
MgO (mg/100g)	177.7	126.5

[a] Organic matter.
[b] Dissolved organic carbon.
[c] Organic carbon.
[d] Cationic exchange capacity.

Characterization of Soil Samples

Soil particle size distribution was determined using the pipette method. Inorganic carbon was determined as $CaCO_3$ with a Bernard calcimeter. Organic carbon (OC) content was calculated as difference between total C (measured with the LECO CN628 elemental analyser) and inorganic carbon. OM was calculated from the OC results multiplied by 1.724 and DOC was determined in a 1:2 (w/v) water extract as indicated for organic amendments. Clay minerals (montmorillonite, illite and kaolinite) were qualitatively identified in the soil clay fraction by the X-ray diffraction technique using a Philips PW1710 diffractometer (Eindhoven, The Netherlands).

Chemical extraction and analysis

The extraction and analysis of herbicides and their major metabolites formed during the experiment was carried out as indicated in Marín-Benito et al. (2019). Briefly, triplicate subsamples of moist soil (6 g) from each 10-cm segment of unamended or amended soil cores taken at each sampling time were extracted with acetonitrile (12 mL), undergoing an ultrasonic bath (1 h, 20 ºC), shaking (24 h, 20 ºC), centrifugation (5045 g, 15 min), and filtration (< 0.45 µm). Extracts (8 mL) were evaporated until dryness at 25 ºC under a nitrogen stream using an EVA-EC2-L evaporator (VLM GmbH, Bielefeld, Germany). The residue was dissolved in 0.75 mL of acetonitrile and transferred to a glass vial for analysis.

The herbicides and their metabolites were determined by HPLC-DAD-MS using a Waters chromatograph (Waters Assoc., Milford, USA) with a Phenomenex Luna (3 µm C18, 150 × 4.6 mm) column. The mobile phase was acetonitrile:water + 1% formic acid (80:10). The flow rate was 0.4 mL min^{-1} and the sample injection volume was 20 µL. The detection by DAD was at 243 nm for chlorotoluron and 232 nm for flufenacet. The positive molecular ions (m/z) [$M+H^+$] monitored with a MS detector were 213.04

for chlorotoluron and 364.03 for flufenacet. The retention times were 6.1 min for chlorotoluron and 7.9 min for flufenacet. Monitoring also involved positive molecular ions (m/z) [$M+H^+$] 198.65 for desmethyl chlorotoluron, and negative molecular ions (m/z) [$M-Na^+$] 274.26 for flufenacet ESA and [$M-H^+$] 224.15 for flufenacet OA, respectively. The limits of detection (LOD) and quantification (LOQ) for flufenacet ranged from 0.003 (S+SMS) to 0.005 µg mL^{-1} (S+GC), and from 0.009 (S+SMS) to 0.016 µg mL^{-1} (S+GC), respectively. In the case of chlorotoluron, the LOD was 0.002 µg mL^{-1} for all the soil treatments, and the LOQ varied between 0.006 (S+GC) and 0.008 µg mL^{-1} (S+SMS). The recoveries of the extraction method were determined by spiking three soil samples in each treatment with analytical grade herbicide to a final concentration of 3 mg kg^{-1}, performing the extraction procedure as described above. The mean recovery values varied between 101% and 115% for chlorotoluron, and 95% and 101% for flufenacet.

Table S3. Initial characteristics of unamended (S) and SMS- and GC-amended (S+SMS and S+GC) soil profiles.

Treatment Depth	Horizon type	Texture	Sand (%)	Silt (%)	Clay (%)	pH	Bulk density ($g\ cm^{-3}$)	$CaCO_3$ (%)	OC[a] (%)	OM[b] (%)	DOC[c] ($mg\ g^{-1}$)	N (%)	C/N	CEC[d] ($cmol_c\ kg^{-1}$)	P_2O_5 (mg/100g)	K_2O (mg/100g)	CaO (mg/100g)	MgO (mg/100g)	Clay mineralogy[e]
S																			
0-10 cm	Ap	sandy loam	80.4	4.7	14.9	6.34	1.48	0.00	0.77	1.33	0.12	0.05	14.7	8.5	2.3	4.7	104.4	17.4	M, I, K
11-30 cm	Ap	sandy loam	79.7	4.9	15.4	6.62	1.45	0.19	0.91	1.57	0.13	0.07	12.4	7.7	1.5	3.9	108.4	19.3	M, I, K
31-55 cm	Bw	sandy loam	77.4	6.0	16.6	7.13	1.54	0.07	0.51	0.88	0.09	0.04	13.8	6.7	0.9	3.9	96.9	17.4	M, I, K
56-90 cm	2B1	sandy loam	72.9	7.4	19.7	7.36	1.61	0.13	0.27	0.47	0.04	0.02	17.3	6.8	0.6	4.4	93.2	17.8	M, I, K
91-160cm	2Bt/C	sandy clay	68.3	9.7	22.0	7.74	1.60	0.14	0.29	0.50	0.03	0.02	12.0	7.5	0.8	4.7	112.0	25.0	M, I, K
S+SMS																			
0-10 cm	Ap	sandy loam	76.7	6.8	16.5	7.11	1.23	1.01	2.64	4.56	0.50	0.24	11.2	10.9	12.6	149.6	512.8	43.7	M, I, K
11-30 cm	Ap	sandy loam	78.8	5.0	16.2	7.15	1.45	0.19	0.95	1.64	0.39	0.07	13.5	7.8	2.8	8.5	142.2	20.2	M, I, K
S+GC																			
0-10 cm	Ap	sandy loam	78.7	4.7	16.6	6.99	1.34	0.00	1.69	2.92	0.38	0.14	12.5	11.0	6.9	30.0	183.0	29.0	M, I, K
11-30 cm	Ap	sandy loam	79.2	4.7	16.1	6.70	1.45	0.19	0.94	1.63	0.27	0.07	13.0	8.3	3.1	5.8	123.6	21.6	M, I, K

[a] Organic carbon.
[b] Organic matter.
[c] Dissolved organic carbon.
[d] Cationic exchange capacity.
[e] M, montmorillonite; I, illite; K, kaolinite

Data Analysis

Standard deviation (SD) was used to indicate variability among replicates. A two-way analysis of variance (ANOVA) was used to compare the effects of the different soil treatments and times on soil characteristics and on bromide and herbicide mobility in the soil profile. Fisher's least significant difference (LSD) was determined at a confidence level of 95%. Simple and multiple linear regression models were used to relate chemical mobility to the OC, DOC and water content of soils. SPSS Statistics v22.0 software for Windows (IBM Inc. Chicago, ILL) was used.

Highlights

- Herbicide concentrations were evaluated in soil profiles for 2 years along with Br^- tracer ion and water content
- Organic residues increased the soil's water-holding capacity and the herbicide adsorption by topsoil
- Herbicide transport increased by soluble organic carbon, initial soil moisture and rainfall
- Leaching, degradation and other processes could be involved in the chemicals' dissipation in soils
- The data set obtained is needed to simulate pesticide environmental fate with leaching models